Computation of Thermodynamic Oxidation Potentials of Organic Solvents Using Density
Functional Theory (DFT)

Xuerong Zhang , James K. Pugh and Philip N. Ross*
*Ernest Orlando Lawrence Berkeley National Laboratory, University of California,
Berkeley, CA 94720.*

Abstract

Ethers and organic carbonates are commonly used as solvents in lithium battery
electrolyte. It is important to determine the oxidation potentials of these organic solvents
due to the high cathode potential (~ 5 V) in many of these batteries. There are significant
variations in the reported oxidation potentials for electrolytes containing these solvents.
The factors contributing to the variation include the type of salt used in the electrolyte,
composition of the electrode and a somewhat arbitrary determination of the oxidation
potential from the anodic cut-off current. We report here the application of Density
Functional Theory (DFT) to calculate solvent oxidation potentials assuming oxidation
occurs via one-electron transfer to form the radical cation. No specific ion-ion, ion-
solvent, or ion-electrode interactions are included. These values are then compared to the
experimental observations. Eleven solvent molecules are studied: 1,2-dimethoxyethane
(DME), tetrahydrofuran (THF), 1,3-dioxolane (DOL), diethylcarbonate (DEC),
dimethylcarbonate (DMC), ethylmethylcarbonate (EMC), ethylenecarbonate (EC),
propylene carbonate (PC), butylene carbonate (BC), vinylene carbonate (VC) and
catechol carbonate. Optimized geometries of the radical cations correlate well with the
fragmentation patterns observed in mass spectrometry. The oxidation potentials of
saturated carbonates are calculated to be approximately 1V higher than the organic
ethers, which is consistent with reported literature values. Quantitative comparison with
experiment will require more careful measurements to eliminate other oxidation reactions
and a standardized procedure for determining the oxidation potential.

Introduction

Aprotic organic solvents are generally employed in commercially available lithium battery electrolyte. The typical operational potential of a lithium battery is between 0 and 5 V, the range of which is beyond the thermodynamic range of most organic solvents.[1] Solvents, therefore, can be reduced and/or oxidized at the negative and positive electrodes during the battery charging process. A fundamental understanding of the redox products and potentials of these organic solvents is crucial in the development of lithium battery technology.

The solvent redox potentials are commonly studied by scanning the potential at an inert electrode, e.g. Pt or Au, and observing the cathodic and/or anodic currents. This provides an indication of the solvent reduction and/or oxidation. The reported values, however, vary significantly and are not clearly established. One factor that may account for these discrepancies is the determination of the correct oxidation potentials by arbitrary criteria for the onset of anodic current.[2-8] Ossola and coworkers summarized the oxidation potentials for several electrolyte solutions from their experimental data and previous literature reports. They observed that the results found with $LiClO_4$ or $LiAsF_6$ solutions are rather scattered and attributed it the uncertainty in oxidation peak determination. It also appears that the electrolyte oxidation potential can be influenced by salt composition. Kanamura[9] observed different oxidation profiles for propylene carbonate (PC) based electrolyte when various salts were employed. When $LiAsF_6$, $LiBF_4$ and $LiPF_6$ were used a large amount of Ni fluorides and oxides were formed on the Ni electrodes and the oxidation of PC was enhanced. Oxidation in the presence of $LiCF_3SO_3$ salt was more suppressed. The same group also reported that the oxidation

potential values of electrolyte varied with the composition of the electrode. [10] The oxidation potential of PC/LiClO$_4$ electrolyte was reported to be 4.2 V vs Li/Li$^+$ on a Ni electrode, 5.6 V on Au or Pt electrodes and 6.0 V on Al electrode. Imhof and Novak[11] studied PC oxidation via differential electrochemical mass spectrometry (DEMS) and CO$_2$ evolution was detected at LiNiO$_2$, LiCoO$_2$ and LiMn$_2$O$_4$ composite electrodes. When using LiNiO$_2$, the gas started to evolve at 4.2 V, lower than the 4.8 V observed on the other two electrodes.

In this work, we present a computational study of both neutral molecules and analogous radical cations using density functional molecular orbital theory (DFT). The solvent oxidation process is assumed to be a one-electron transfer from a solvent molecule to the electrode, leaving a substrate radical cation. Experimentally radical cations can be generated in the gas phase by the technique of electron bombardment in electron impact mass spectrometry (EIMS). Much insight into the rearrangement and degradation mechanisms of oxidized species can be obtained from the mass spectrometry fragmentation patterns. Therefore it seemed logical to compare the geometric results from DFT calculations of neutral and radical cation species to the mass spectrometry fragmentation patterns found in the literature. In this paper we report the initial and possible final oxidation products for eleven solvent molecules as well as their oxidation potential values calculated from thermodynamic energy cycles.

Computational Methodology:

Starting geometries at the PM3[12] level were obtained with the P.C. Spartan Pro[13] program run on a Pentium class personal computer and the Windows 95 operating system. Files were then exported in protein data bank (PDB) format to Gaussian 98W.[14]

Full geometry optimizations and frequency calculations were performed at the b3lyp/6-31+g(d)[15] level. Each species was found to be minima by having no negative eigenvalues in the frequency calculation. The density functional method employed uses the Becke three parameter functional[16] combined with the correlation functional of Lee, Yang and Parr.[17] This method provides a better energetic description through the use of electron correlation. The 6-31+G(d) basis set includes both diffuse[18] and polarization[19] functions on all heavy atoms. For the following discussion only the b3lyp/6-31+g(d) results will be used. The total free energies of gas phase molecules and ions were corrected for vibrational energies (298.3 K).

The solvation energy for the radical cations was conducted utilizing the PCM Model[20] at the B3LYP/6-31+G(d) level. The PCM model is a Self-Consistent Reaction Field (SCRF) method, which models the solvent as a continuum of uniform dielectric constant. It should be noted that PCM model in Gaussian 98 provides the free energy of solvation, not just the enthalpy of solvation[21]. We assumed a common supporting electrolyte for all the solvation calculations, $\varepsilon=78$, an intermediate value between the dielectric constant of PC (64.4) and EC (89.2). Both PC and EC have relatively high oxidation potentials and thus would compose a suitable supporting electrolyte for subsequent experiments aimed at confirming the oxidation potentials reported here. The radical cations are assumed to be solvated by the supporting solvent in the electrolyte rather than by the parent molecule. This assumption will make comparison of the absolute values of the reduction potentials with experiment more difficult, but there are at present no definitive experimental values with which to compare. Using a common supporting solvent does, however, improve the accuracy of the *relative values* of the

calculated reduction potentials, and these are also important values from a practical standpoint. Furthermore, solvents with low dielectric constants are usually used as co-solvents rather than alone. Also, since heats of vaporization are not available for all the solvents of interest, the vaporization energies of all solvents are assumed to be the same as that for PC.

Results and Discussion:

The calculated structural parameters for the optimized gas phase solvent molecules and their ions are tabulated in Table 1 to 4. Also tabulated there are the differences in electronic energy between the neutral solvent and the ion before zero point energy correction (ΔE). Table 5 summarizes the calculated Gibbs free energy of ionization, the free energy of solvation of the radical cations in PC solvent, the free energy of formation of the solvated ions, and the calculated electrochemical potential of oxidation. Also given in Table 5 is a comparison of the calculated potentials with experimental values reported in recent literature (1988 or later). The results before 1988 were summarized in Ossola's paper[22]. It should be noted that the experimental oxidation potentials are not thermodynamic potentials, only estimates of thermodynamic potentials based on kinetic measurements. The calculated oxidation potential values are therefore expected to be lower than the experimental values.

Ether Solvents:

Organic ethers are often employed as the solvent in electrolytes for lithium secondary batteries. Representative organic ethers used for this purpose are 1,2-dimethoxyethane (DME), tetrahydrofuran (THF) and 1,3-dioxolane (DOL). For each of these, the highest

occupied molecular orbital (HOMO) would correspond to an orbital that contains the non-bonded electrons of oxygen.
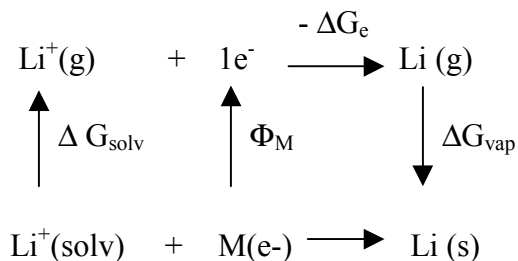
1. Tetrahydrofuran (THF):

The geometric changes upon oxidation of THF are small and can be explained simply by the effect of the positive charge on oxygen upon loss of one electron. This would create a movement of electron density from the adjacent carbons and subsequent shortening of the C-O bonds. Another possibility would be hyperconjugation from α C-H bonds. There is a lengthening of the C-H bonds of ~ 0.014 Å that would indicate some hyperconjugation with the adjacent positive center (Table 1a).

The EIMS of THF has a maximum abundance peak that corresponds to the radical cation of cyclopropane[23-25] (Scheme I). Upon the formation of the cyclopropane radical cation there is a loss of formaldehyde – a gaseous byproduct. Any gas formation during the operation of a battery is detrimental to the system due to the increased pressure in the closed cell.

To determine the electrochemical oxidation potential of solvents we use thermodynamic chemical cycles[26] for both the lithium electrode reaction (the reference potential) and the THF molecule oxidation reaction.
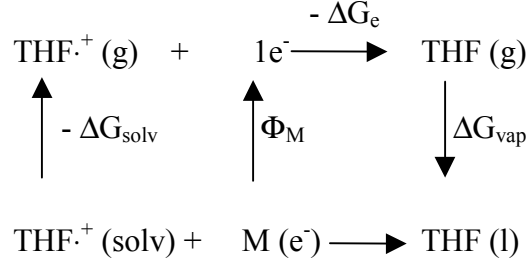
For the Li/Li^+ reference:

$$Li^+(g) \quad + \quad 1e^- \quad \xrightarrow{-\Delta G_e} \quad Li\,(g)$$

$$\Delta G_{solv} \uparrow \qquad \Phi_M \uparrow \qquad \downarrow \Delta G_{vap}$$

$$Li^+(solv) \quad + \quad M(e\text{-}) \quad \longrightarrow \quad Li\,(s)$$

and the free energy for Li/Li^+ reduction is therefore given by the quantities:

$$\Delta G_{ref} = \Delta G_{solv} (Li^+) + \Phi_M - \Delta G_e (Li) - \Delta G_{vap} (Li) \tag{1}$$

where $\Delta G_{solv} (Li^+)$ is the free energy of solvation of Li^+ in PC, Φ_M is the work function of

the inert metal electrode, $\Delta G_e (Li)$ is the calculated free energy of ionization of Li, and

$\Delta G_{vap} (Li)$ is the free energy of vaporization of Li.

For THF oxidation:

$$THF\cdot^+ (g) \; + \; 1e^- \xrightarrow{\; -\Delta G_e \;} THF (g)$$

$$\uparrow -\Delta G_{solv} \qquad \uparrow \Phi_M \qquad \downarrow \Delta G_{vap}$$

$$THF\cdot^+ (solv) + \; M (e^-) \longrightarrow THF (l)$$

and the free energy for THF oxidation is given by the quantities:

$$\Delta G_{THF / THF\cdot}{}^+ = - \Delta G_{vap} + \Phi_M - \Delta G_e (THF) - \Delta G_{solv} (THF\cdot^+) \tag{2}$$

where ΔG_{vap} is the free energy of solvent vaporization, ΔG_e is the free energy of

ionization of the THF molecule, and $\Delta \mathbf{G}_{solv} (THF\cdot^+)$ is the solvation energy of the radical

cation in PC solution. Note all of the thermodynamic quantities in eqns 1 and 2 are the

absolute values, i.e. whether the process is endothermic or exothermic is accounted for in

the thermodynamic cycle. This sign convention is adopted throughout the paper. The

oxidation potential of THF versus the Li/Li^+ reference electrode is derived from the

difference between equation (1) and (2):

$$E°_{THF / THF\cdot}{}^+ = (\Delta G_{THF / THF\cdot}{}^+ - \Delta G_{ref}) / F$$

$$= (1/F) \; [- \Delta G_{vap} - \Delta G_e (THF) - \Delta G_{solv} (THF\cdot^+) + \Delta G_e (Li) + \Delta G_{vap} (Li) - \Delta G_{solv}$$

$$(Li^+)] \tag{3}$$

Note that as expected the standard reduction potential is independent of the work function

of the electrode material. The $\Delta G_{vap} (Li)$ is tabulated quantity[27] of 118.0 kJ/mol. ΔG_{vap} is

25 kJ/mol[27]. ΔG_{solv} (Li$^+$) and ΔG_{solv} (THF$^{\cdot+}$) in PC was calculated by DFT to be 403.6 and 243.8 kJ/mol respectively. ΔG_e (Li) and ΔG_e (THF) molecule were calculated to be 544.2 and 879.3 kJ/mole respectively. Using this procedure, the oxidation potential for THF is determined to be 4.35 V. This value is in good agreement with the literature value of $\geq$ 4 V reported by Campbell et al[28].

2. 1,2-Dimethoxyethane (DME):

The calculations of the DME radical cation give a C1-C2 bond lengthening of 0.15 Å and a shortening of both the C1 and C2 carbon-oxygen bonds of 0.06 Å (Table 1b). The α-cleavage mechanism of aliphatic ethers in mass spectrometry is a common fragmentation [29,30] and would account for the lengthening of the carbon-carbon bond. The EI mass spectra of DME gives the highest relative abundance fragment[31] that corresponds to the ion left after carbon-carbon bond cleavage. As the calculated radical cation geometry is symmetrical it can be represented by the following delocalized structure:
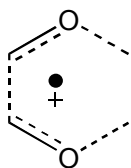

Scheme II outlines the geometry of the radical cation and the mechanism for fragmentation. Homolytic bond cleavage of the C1-C2 bond would fragment the molecule into a separate radical and cation species. The newly formed radical center is α to an oxygen atom. Orbital interaction with a non-bonded electron pair creates a more stable radical as shown diagrammatically in Scheme III. In this interaction there is an overall stabilization due to two electrons having a lower energy while only one is raised.[32]

The methoxymethyl radical is likely to undergo a hydrogen abstraction reaction and form dimethyl ether. A coupling reaction from this radical would lead to the parent compound. Any nucleophilic species could react with the cationic species. The potential calculated for oxidation of DME to its radical cation is 4.11 V, close to the reported value of 4.6 V by Ossola[22].

3. 1,3-Dioxolane:

In the optimized radical cation, the C2-O bond lengths are shorter and O1-C5, O3-C4 bonds longer by 0.04 and 0.05 respectively (Table 1c). As with DME the structure is also symmetric and can be represented by a resonance-delocalized cation:
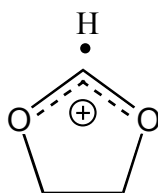

Consistent with this structure is the lengthening of the methylene C-H bonds of 0.04 Å. The EIMS of 1,3-dioxolane exhibits the loss of a hydrogen atom as the main fragmentation process[33] and correlates with the computational results (Scheme IV.) The oxidation potential of DOL in PC is calculated to be 4.17 V (Table 5). All three ethereal solvents were calculated to have low oxidation values around 4 V, which made them less desirable in a high voltage battery such as lithium-ion batteries.

Linear Carbonates:

The three linear carbonates studied: dimethylcarbonate (DMC), diethylcarbonate (DEC) and ethylmethylcarbonate (EMC) all have optimized geometries with similar properties (Table 2). In each the carbonyl carbon - oxygen bond is lengthened, the carbonyl carbon – ether oxygen bond is shortened and the alkyl carbon – ether oxygen bond is lengthened.

The best representation is the delocalized structure shown below and the resonance structures depicted in Scheme V:
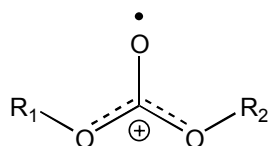

The mass spectrum of DMC is unique among alkyl carbonates because it has a distinguishable parent ion and the rearrangement commensurate with carbon dioxide expulsion is pronounced[34] (Scheme VI). As mentioned before, any mechanism that leads to gas formation may be detrimental to the battery cell. Although CO_2 loss can occur in all alkyl carbonates, particularly those that contain a methyl substituent, it is far more likely for α-cleavage of an ether C-O bond[35] to be the major degradation pathway (Scheme VII.). DEC should then decompose via α-cleavage while EMC could have aspects of both mechanisms. The calculated oxidation potentials for these linear carbonates are between 5.5 to 5.6 V.

Cyclic Carbonates

Ethylene carbonate (EC), propylene carbonate (PC) and trans-butylene carbonate (BC) are representative cyclic carbonates. Each of these contains a five-membered ring. The presence of a parent ion – CO_2 peak in the mass spectra of ethylene carbonate suggests a rearrangement involving a hydrogen transfer and loss of carbon dioxide[36] (Scheme VIII). This same rearrangement mechanism has been seen in the mass spectra of butylene carbonate[37] and is expected to occur in propylene carbonate as well. Our calculations for ethylene carbonate reproduce these results. There is an apparent carbonyl carbon – ether oxygen bond breaking (Table 3b). This clearly demonstrates the molecule is on route to the loss of CO_2. The optimized structures for both propylene

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carbonate and butylene carbonate more closely match the delocalized structure shown below (Table 3a, 3c):
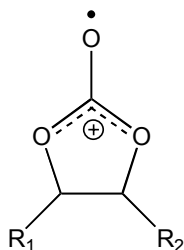
$R_1 = CH_3$; $R_2 = H$ for PC
R_1, $R_2 = CH_3$ for BC

This is likely due to the inductive stabilization of the methyl substituents toward positive charge. It is clear, however, from the lengthening of the carbon oxygen bonds that the same fragmentation and loss of CO_2 is also likely with these species.

EC is calculated to be the most stable against oxidation, with an oxidation potential as high as 5.58 V vs Li/Li$^+$. The calculated oxidation potentials for the other two saturated cyclic carbonates PC and BC are 5.61 and 5.51 V respectively.   The experimental value of PC oxidation potential is ranged from 5.2 V[22] to 6.0 V[38]. Ossola[22] demonstrated that the oxidation profile of PC-LiClO$_4$ had a long tail that made it uncertain in the determination of the starting potential. The oxidation potentials for the saturated carbonates are calculated to be ca 1 V more positive than for the ethers, in oxidation. This result is consistent with the study done by Campbell on THF and PC solvents[28].

Unsaturated Cyclic Carbonates

Vinylene carbonate (VC) and catechol carbonate (CC) are two representative examples of unsaturated carbonates used as additives in PC-based electrolyte for lithium-ion batteries. It was suggested that these additives suppress co-intercalation of PC into

the carbonaceous electrode.[39,40] Both of these molecules exhibit similar geometric changes

upon oxidation. There is a shortening of the original carbonyl C-O bond, a lengthening

of the adjacent C-O ether bonds and a lengthening of the double bond of the five

membered carbonate containing ring (Table 4.) Mechanistically this would lead to the

expulsion of carbon monoxide and formation of a dione species. This is shown for both

molecules in Scheme IX. The calculated oxidation potentials, however, are found to be

similar to those of the ethers and lower than the saturated carbonates by ca. 1 V. Similar

to ethers, the relatively low oxidation potentials of these two unsaturated carbonates

could limit their effectiveness in lithium-ion batteries. Wang et al.[39] reported, however,

that no significant oxidation of CC was observed on a $LiCoO_2$ electrode up to 4.3 V vs.

Li^+/Li.

Summary:

The energetics of solvent oxidation was studied by the density functional theory

assuming an oxidation process of one-electron transfer from a solvent molecule to an

inert electrode to form a radical cation. Optimized geometries of the radical cations

correlate well with the fragmentation patterns observed in mass spectrometry.   The

absolute values of the thermodynamic potentials for solvent oxidation are, however,

subject to greater uncertainty due to the simplified solvation model and neglect of

specific ion-ion or ion-solvent interactions. Furthermore, it is difficult to compare the

calculated potential values to the experimental values because of a lack of a standard

procedure for the measurement of the oxidation potential. A complicating factor is

oxidation of the salt used in the electrolyte, and the observed oxidation potential of the

electrolyte may not reflect the solvent oxidation. These calculations were aimed primarily

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at providing a self-consistent analysis of the oxidation chemistry of common solvent molecules. The *relative* values should provide a reasonable indication of the difference in oxidation potentials if oxidation takes place via a one-electron transfer process. Oxidation potentials that are significantly, e.g. > 1.0 V, lower than the calculated value are probably indicative of a different reaction pathway. The oxidation potentials of saturated carbonates were calculated to be approximately 1V higher than the organic ethers, which is consistent with the literature values.[22,28] Quantitative comparison with experiment will require more careful measurements to eliminate other oxidation reactions and a standardized procedure for determining the oxidation potential.

Acknowledgement

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Table 1. Calculated structural parameters and energy for ethers: a) Tetrahydrofuran (THF,1), b) Dimethoxy ethane (DME, 2), and c) Dioxolane (DOL, 3) and their radical cations (THF$^{\cdot+}$, DME$^{\cdot+}$ and DOL$^{\cdot+}$) using DFT method. Bond lengths are in (Å).

a)

	THF	THF$^{\cdot+}$
C1-O	1.44	1.43
C4-O	1.44	1.43
C1-C2	1.53	1.52
C2-C3	1.54	1.55
C3-C4	1.53	1.52
Symmetry	C1	C1
ΔE (kJ/mol)	0	887.2

b)

	DME	DME$^{\cdot+}$
C1-O1	1.42	1.44
C2-O1	1.42	1.36
C2-C3	1.52	1.67
C3-O2	1.42	1.36
O2-C4	1.42	1.44
Symmetry	C1	C1
ΔE (kJ/mol)	0	840.9

c)

	DOL	DOL$^{\cdot+}$
C1-O1	1.40	1.36
C1-O2	1.40	1.36
C2-O2	1.41	1.46
O1-C3	1.41	1.46
C3-C2	1.52	1.54
Symmetry	C1	C1
ΔE (kJ/mol)	0	915.6

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Table 2: Calculated structural parameters and energy for linear carbonate, carbonate (DEC,7), ethyl methyl carbonate (EMC,8), dimethyl carbonate (DMC,9) and their radical cations (DEC$\cdot^{+}$, EMC$\cdot^{+}$, and DMC$\cdot^{+}$) using DFT methods. Bond lengths are in (Å).

a)

	DEC	DEC$\cdot^{+}$
C1=O1	1.21	1.31
C1-O2	1.35	1.28
C1-O3	1.34	1.27
O2-C2	1.45	1.53
O3-C3	1.45	1.53
C2-C4	1.52	1.51
C3-C5	1.52	1.51
Symmetry	C1	C1
ΔE (kJ/mol)	0	954.6

b)

	EMC	EMC$\cdot^{+}$
C1=O1	1.21	1.30
C1-O2	1.35	1.28
C1-O3	1.34	1.27
O2-C2	1.45	1.54
O3-C2	1.45	1.49
C3-C4	1.52	1.50
Symmetry	C1	C1
ΔE (kJ/mol)	0	970.5

c)

	DMC	DMC$\cdot^{+}$
C1=O1	1.18	1.30
C1-O2	1.32	1.27
C1-O3	1.32	1.28
O2-C2	1.43	1.50
O3-C3	1.43	1.50
Symmetry	C1	C1
ΔE (kJ/mol)	0	987.2

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Table 3: Calculated structural parameters and energy for saturated cyclic carbonates: a) propylene carbonate (PC,4), b) ethylene carbonate (EC,5); and c) butylene carbonate (BC,6) and their radical cations (PC·$^+$, EC·$^+$, and BC·$^+$) using DFT method. Bond lengths are in (Å).

a)

	PC	PC·$^+$
C1=O1	1.20	1.29
C1-O2	1.36	1.29
C1-O3	1.36	1.28
C2-O2	1.44	1.50
C3-O3	1.45	1.54
C2-C3	1.54	1.54
C3-C4	1.52	1.51
Symmetry	C1	C1
ΔE (kJ/mol)	0	1003.3

b)

	EC	EC·$^+$
C1=O1	1.20	1.16
C1-O2	1.36	1.29
C1-O3	1.36	1.73
C2-O2	1.44	1.45
C3-O3	1.43	1.36
C2-C3 (e)	1.53	1.54
Symmetry	C1	C1
ΔE (kJ/mol)	0	1064.3

c)

	BC	BC·$^+$
C1=O1	1.20	1.29
C1-O2	1.36	1.28
C1-O3	1.36	1.28
C2-O2	1.45	1.53
C5-O3	1.45	1.53
C5-C2	1.54	1.54
C3-C2	1.52	1.51
C5-C4	1.52	1.51
Symmetry	C1	C1
ΔE (kJ/mol)	0	983.7

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Table 4. Calculated structural parameters and energy for saturated cyclic carbonates: a) catachol carbonate (CC,10), and b) vinylene carbonate (VC,11) and their radical cations (CC$\cdot^+$, and VC$\cdot^+$) using DFT method. Bond lengths are in (Å).

a)

	CC	CC$\cdot^+$
C1=O1	1.19	1.17
C1-O2	1.38	1.41
C1-O3	1.38	1.41
C2-O2	1.38	1.34
C7-O3	1.38	1.34
C3-C2	1.38	1.39
C6-C7	1.38	1.39
C4-C3	1.41	1.39
C5-C6	1.40	1.39
C4-C5	1.40	1.45
C2-C7	1.39	1.44
Symmetry	C1	C1
ΔE (kJ/mol)	0	860.9

b)

	VC	VC$\cdot^+$
C1=O1	1.19	1.17
C1-O2	1.37	1.42
C1-O3	1.37	1.42
C2-O2	1.39	1.32
C3-O3	1.39	1.32
C2-C3 (e)	1.33	1.41
Symmetry	C1	C1
ΔE (kJ/mol)	0	921.0

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Table 5 Summary of the calculated free energy (ΔG_e) of ionization of the solvent molecule, the free energy of solvation of radical cations in PC solvent (ΔG_{solv}), Gibbs free energy (ΔG_{rxn}) in kJ/mole for formation of the solvated ions, and the calculated electrochemical potential (V) for oxidation of these solvents.

	ΔG_e	ΔG_{solv}	ΔG_{rxn}	E°_{oxd} (vs. Li/Li$^+$)	
				Calculation	Experimental (literature)
EC	1040.0	285.7	-538.1	5.58	6.7 [a]
BC	977.8	229.7	-531.8	5.51	
PC	998.0	240.6	--541.4	5.61	5.2 – 5.6[b], 6.0[a]
EMC	958.7	206.8	-535.7	5.55	6.2 - 6.7[c]
DEC	941.3	198.0	-527.1	5.46	
DMC	977.9	224.2	-542.0	5.62	5.8 - 6.7[d]
DOL	902.9	284.1	-402.6	4.17	
THF	879.3	243.8	-419.3	4.35	≥ 4[e]
DME	836.6	224.2	-396.2	4.11	4.6 [b]
VC	917.6	310.1	-391.3	4.06	
CC	855.4	231.3	-407.9	4.23	

a. Glassy carbon as working electrode and 1.0 M Et$_3$MeN$^+$PF$_6^-$ in solvent.[38]
b. Glassy carbon or Pt as working electrode and LiClO$_4$ as salt.[22]
c. Glassy carbon as working electrode and 1.0 M Et$_3$MeN$^+$PF$_6^-$ in PC/EMC mixture (lower value) and EC/EMC mixture.(higher value) [38]
d. Glassy carbon as working electrode and 1.0 M Et$_3$MeN$^+$PF$_6^-$ in PC/DMC mixture (lower value) and EC/DMC mixture.(higher value) [38]
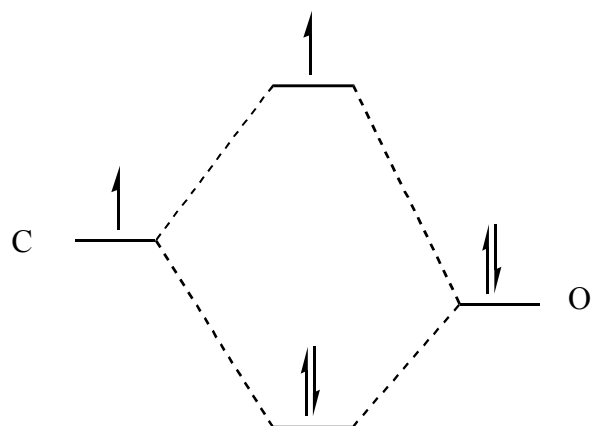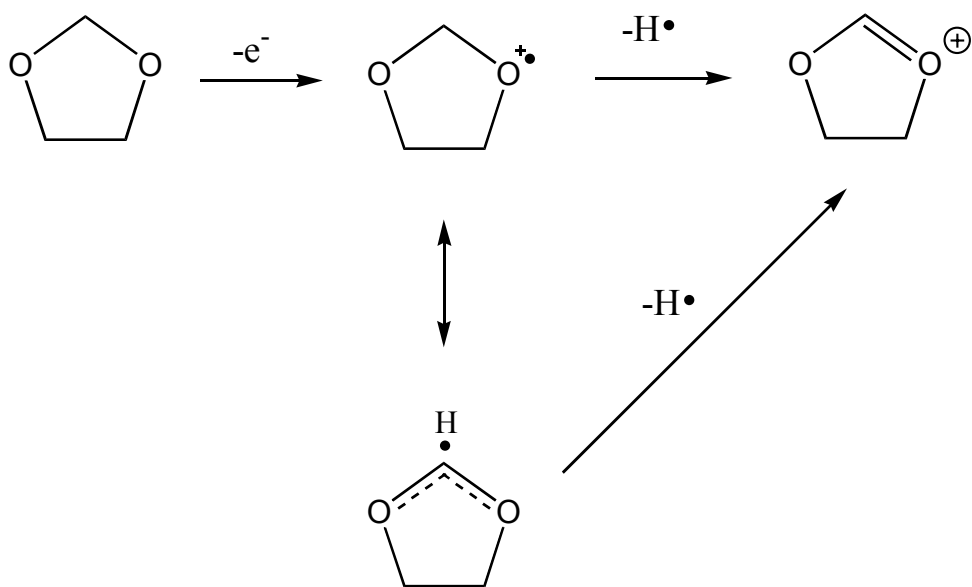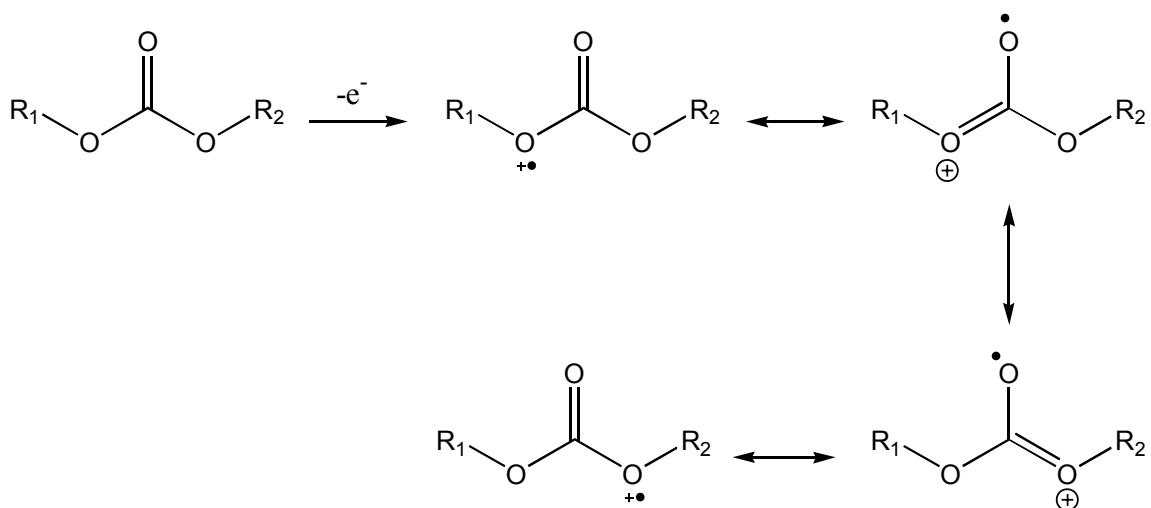e. Used Pt microelectrode and neat solvents without electrolyte.[28]

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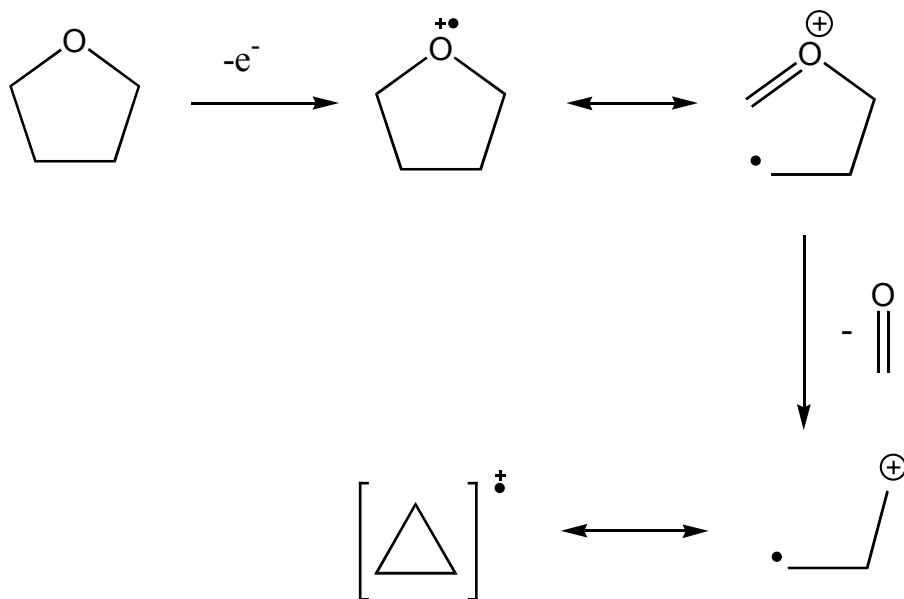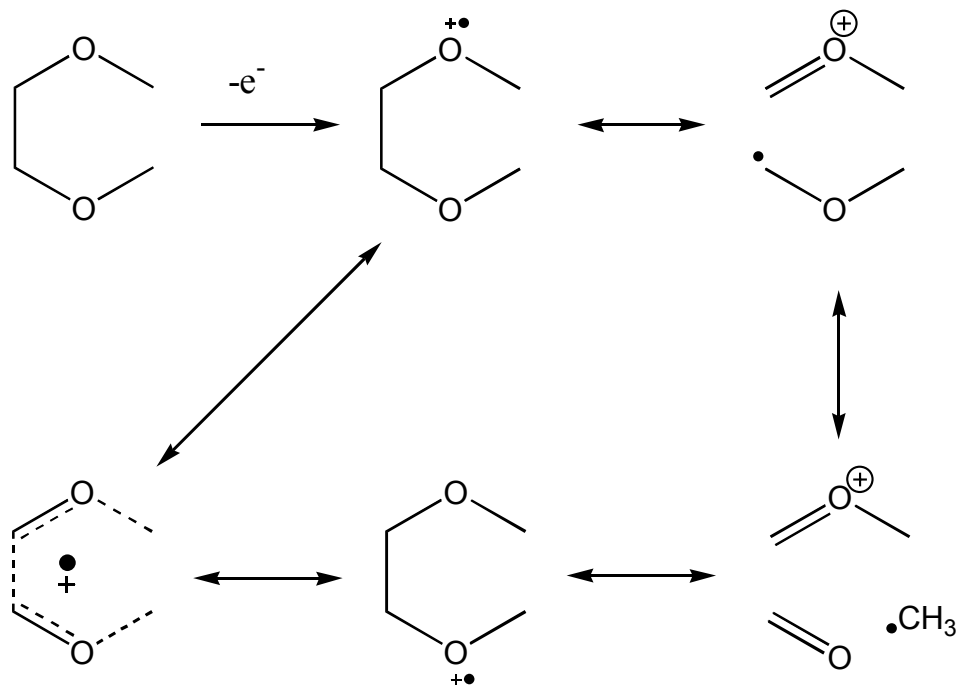
Scheme I

Scheme II
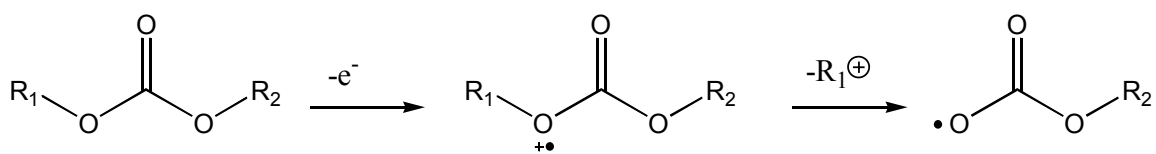
Scheme III

Scheme IV

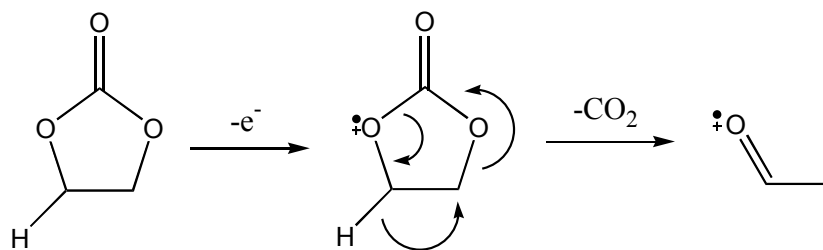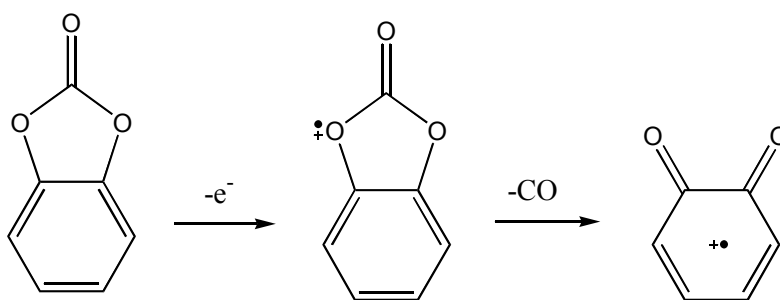## Scheme V
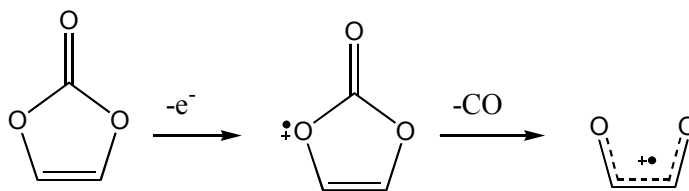

Scheme VI
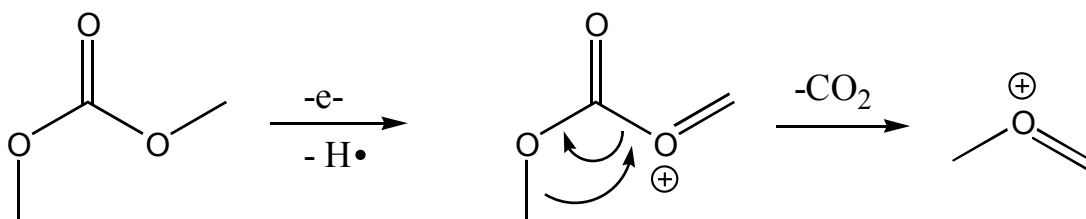
Scheme VII

Scheme VIII

Scheme IX

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